241 Chem

CH-2

Alcohols

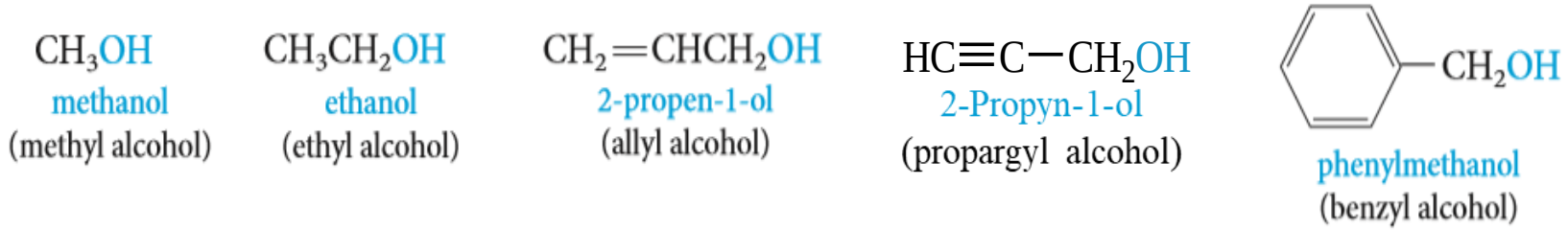
Learning Objectives

By the end of this chapter the student will:

- Know the structure of alcohols
- Know the different classes of alcohols.
- Know the nomenclature of Alcohols
- Know the physical Properties.
- Know the acidity of Alcohols.
- Know the different methods of preparation of Alcohols .
- Know the chemical reactions of Alcohols

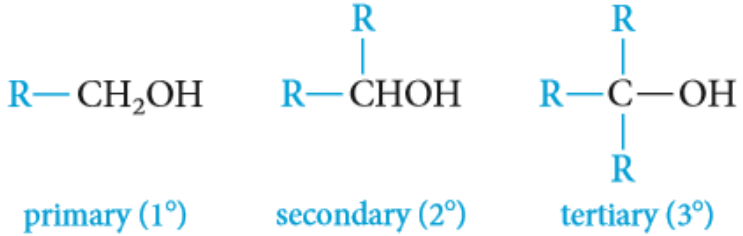
Structural Characteristic of Alcohols

- Alcohols, a class of compounds containing the hydroxyl group (OH)
- Alcohols have a hydroxyl (OH) group bonded to a saturated carbon atom.
- The alcohol carbon atom may be part of a simple alkyl group, an alkenyl or the carbon atom may be a saturated carbon atom that is attached to a benzene ring:

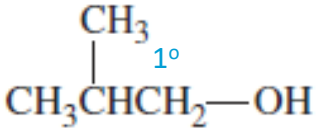


Classification of Alcohols

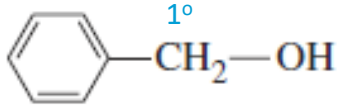
- Alcohols are classified as primary (1º), secondary (2º), or tertiary (3º), depending on whether one, two, or three organic groups are connected to the hydroxyl-bearing carbon atom.
- The carbon atom which connected to the hydroxyl group called carbinol carbon.
- Methyl alcohol, which is not strictly covered by this classification, is usually grouped with the primary alcohols.



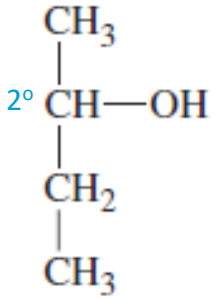
Example:



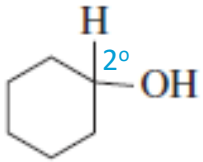
2-methylpropan-1-ol



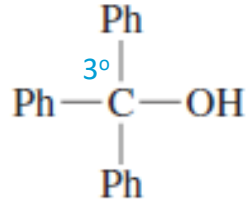
benzyl alcohol



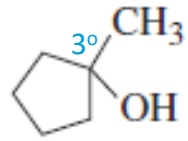
butan-2-ol



cyclohexanol



triphenylmethanol



1-methylcyclopentanol

Nomenclature of Alcohols

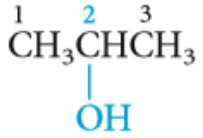
- Common names derived by naming the *alkyl group* followed by the word *alcohol*.
- The IUPAC system: select the longest carbon chain that contains the -OH group as the parent alkane and numbered from the end closer to OH. change the suffix *-e* of the parent alkane to *-ol*
- use a number to show the location of the OH group.
- If there is a functional group suffix and a substituent, the functional group suffix gets the lowest possible number.
- For cyclic alcohols, numbering begins with the carbon bearing the OH group. The OH group is known to be on carbon 1 of the ring.
- In complex alcohols, the number for the hydroxyl group is often placed between the infix and the suffix.
- So the compound containing two hydroxyl groups is named as a *diol* , one containing three hydroxyl groups as a *triol* , and so on.
- Compounds containing OH and C=C groups are often referred to as unsaturated alcohols. choose the chain that include them both even if this is not the longest chain.
- The IUPAC system: the double bond is shown by changing the infix of the parent alkane from *-an-* to *-en-* and the hydroxyl group is shown by changing the suffix of the parent alkene from *-e* to *-ol.*
- Numbers must be used to show the location of both the carbon-carbon double bond and the hydroxyl group.

Nomenclature of Alcohols

methanol
(methyl alcohol)

ethanol
(ethyl alcohol)

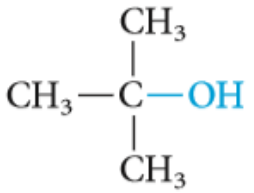
1-propanol
(*n*-propyl alcohol)



2-propanol
(isopropyl alcohol)

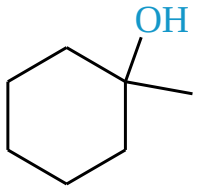
2-butanol
(*sec*-butyl alcohol)

2-methyl-1-propanol
(isobutyl alcohol)



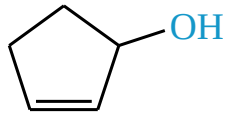
2-methyl-2-propanol
(*tert*-butyl alcohol)

cyclohexanol
(cyclohexyl alcohol)

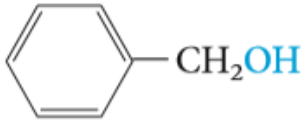


1-Methyl-cyclohexanol

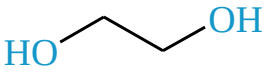
2-propen-1-ol
(allyl alcohol)



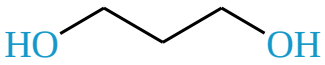
Cyclopent-2-enol



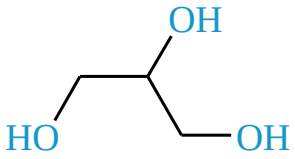
phenylmethanol
(benzyl alcohol)



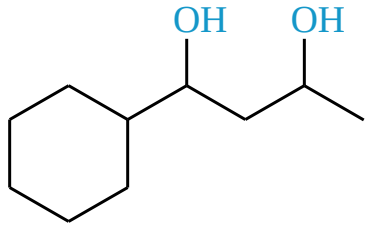
Ethane-1,2-diol
(Ethylene glycol)



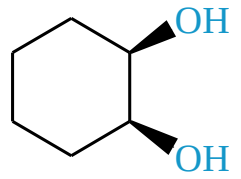
Propane-1,3-diol
(Trimethylene glycol)



Propane-1,2,3-triol
(Glycerol)



1-Cyclohexyl-butane-1,3-diol



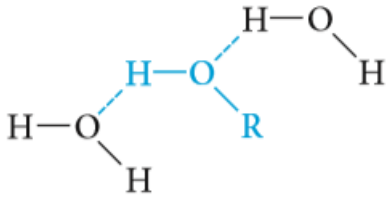
cis-Cyclohexane-1,2-diol

Physical Properties of Alcohols

- Most of the common alcohols, up to about 11 or 12 carbon atoms, are liquids at room temperature.
- Methanol and ethanol are free-flowing volatile liquids with characteristic fruity odors.
- The higher alcohols are viscous, and some of the highly branched isomers are solids at room temperature.
- The higher alcohols have heavier but still fruity odors.

Solubility

- Water and alcohols have similar properties because they all contain hydroxyl groups that can form hydrogen bonds.
- Several of the lower-molecular-weight alcohols as CH_3OH to C_3H_7OH are miscible (soluble in any proportions) with water.



- The solubility decreases as the alkyl group becomes larger.
- The number of hydroxyl groups increases so the solubility increases.

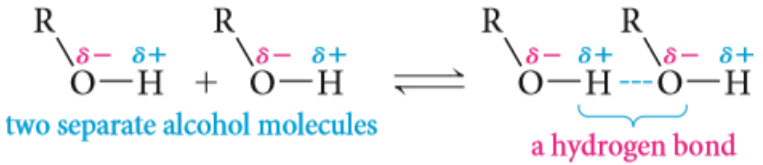
Physical Properties of Alcohols

Boiling Points

- The boiling points of alcohols are much higher than those of ethers or hydrocarbons with similar molecular weights.

	CH_3CH_2OH	CH_3OCH_3	$CH_3CH_2CH_3$
mol wt	46	46	44
bp	+78.5°C	−24°C	−42°C

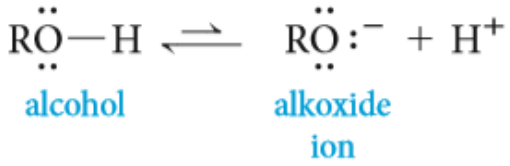
- Alcohol molecules can associate with each other through hydrogen bonding, whereas those of ethers and hydrocarbons cannot.



- The boiling points increase with the increase of the number of OH groups .
- The boiling point decreases with increase in branching in the alkyl group.
- Boiling points of 1° alcohol > 2° alcohol > 3° alcohol.

Physical Properties of Alcohols

Acidity of Alcohols



- Alcohols can function as both weak acids (proton donors) and weak bases (proton acceptors).A strong base can remove the hydroxyl proton to give an alkoxide ion (for example, methoxide ion from methanol, ethoxide ion from ethanol, and so on).
- Electron-withdrawing groups increase acidity by stabilizing the conjugate base.
- Electron-donating groups decrease acidity because they destabilize the conjugate base.
- The order of acidity of various liquid alcohols generally : water > 1^o>2^o>3^o

Relative Acidity

$$H_2O > ROH > RC{\equiv}CH > H_2 > NH_3 > RH$$

Relative Basicity

$$R^- > NH_2^- > H^- > RC{\equiv}C^- > RO^- > HO^-$$

Preparation Of Alcohols

1. Preparation of alcohols via alkenes
    - Oxidation reaction
    - Addition reaction
2. Preparation of alcohols via alkyl halides (*Nucleophilic Substitution*)
3. Preparation of alcohols via Grignard reagents with:

    Aldehydes, Ketones, Esters and Epoxides

4. Preparation of alcohols via Reduction reaction of:

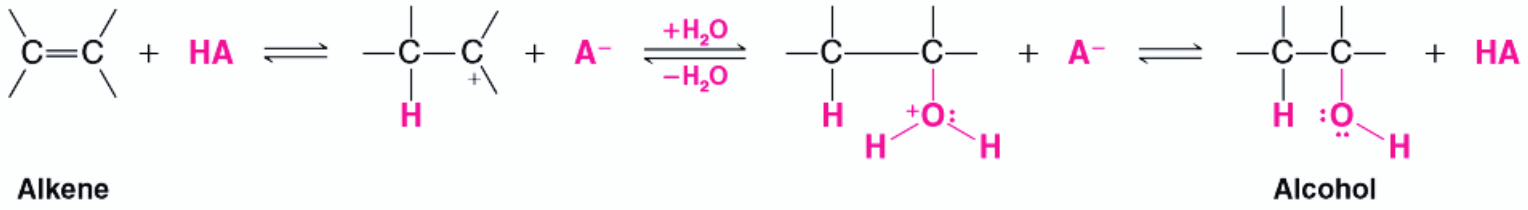
    Aldehydes, Ketones, Acids and Esters

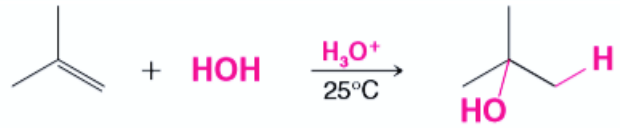
Preparation Of Alcohols

1- Preparation of alcohols via alkenes

a) Acid-Catalyzed Hydration of Alkenes: Addition of water to alkenes

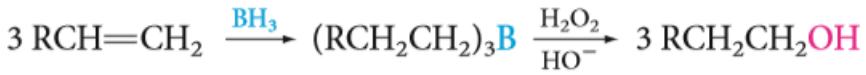
Markovnikov Hydration

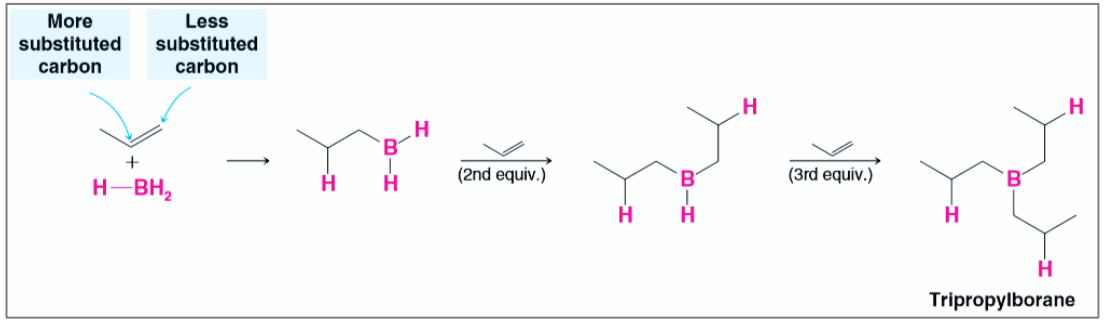




2-Methylpropene (isobutylene) — 2-Methyl-2-propanol (*tert*-butyl alcohol)

Anti-Markovnikov Hydration : Hydroboration–Oxidation:

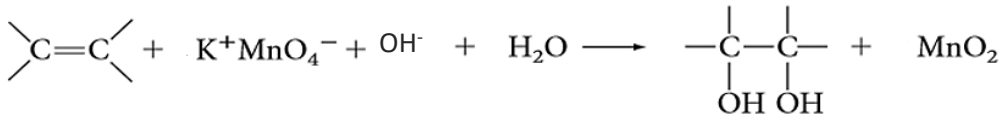


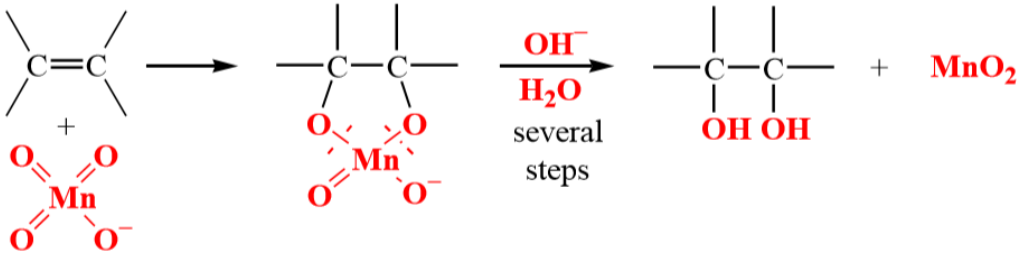


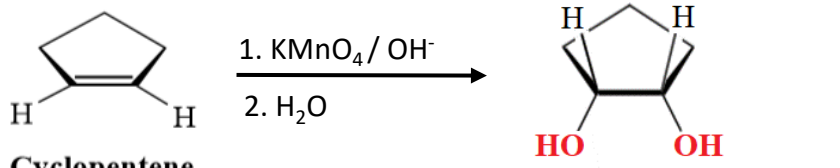
Preparation Of Alcohols

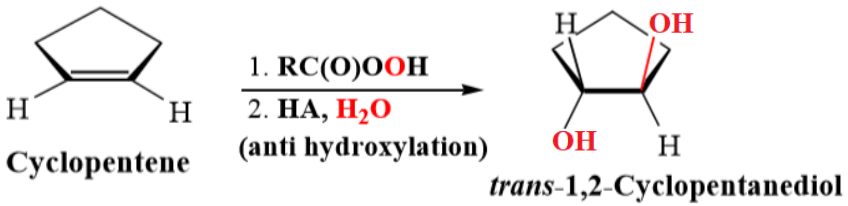
b) Oxidation of alkenes: Synthesis of 1,2-diols

1,2-dihydroxylation

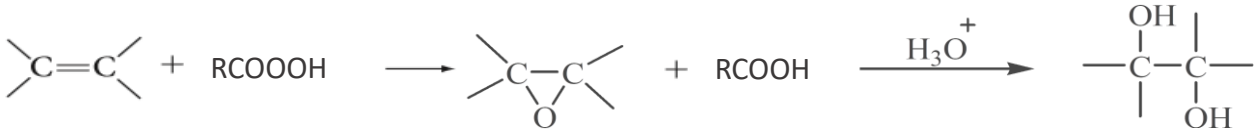


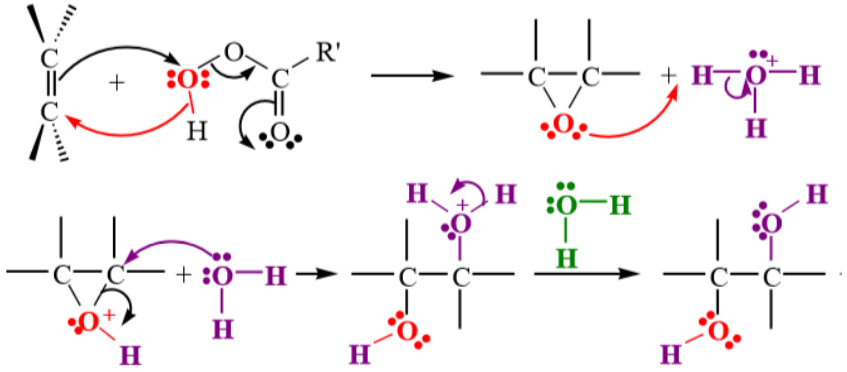


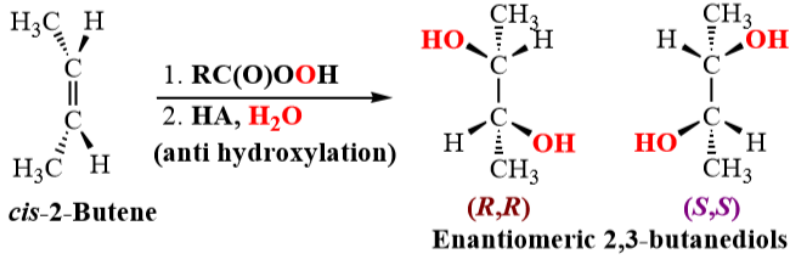


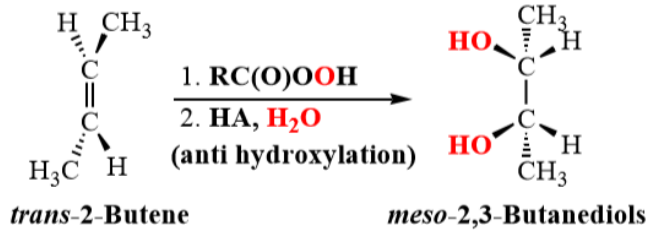


Anti-1,2-dihydroxylation





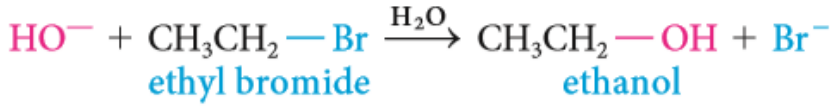


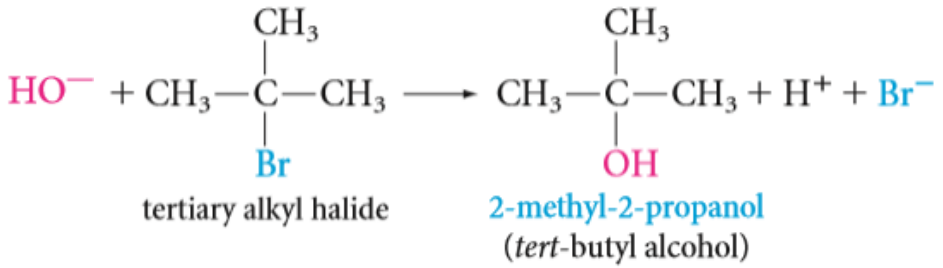


Preparation Of Alcohols

2- Preparation of alcohols via alkyl halides: Hydrolysis of alkyl halides

Nucleophilic Substitution Reactions (S_N1 and S_N2)

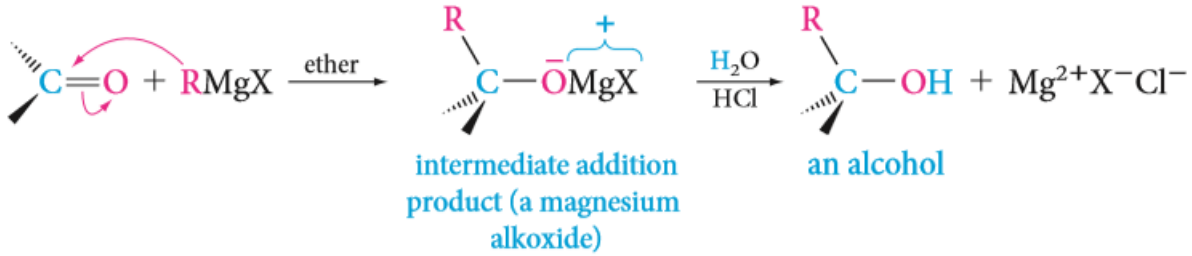


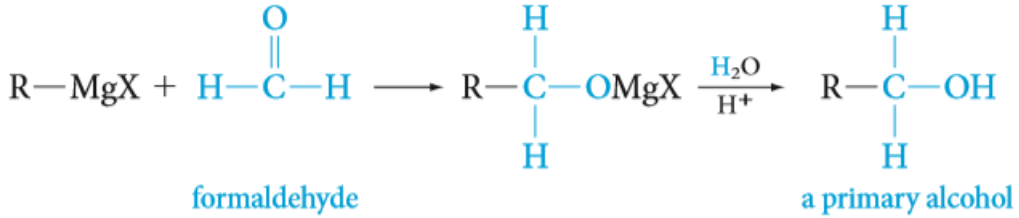


Preparation Of Alcohols

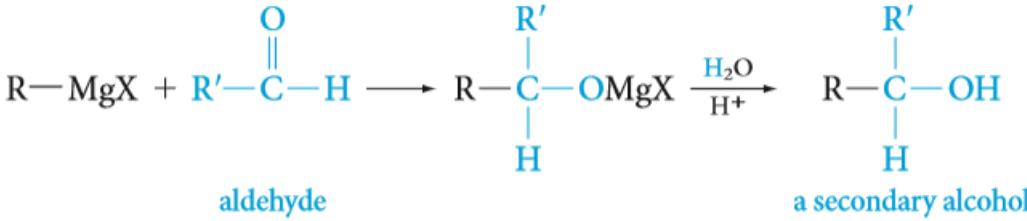
3- Preparation of alcohols via Grignard reagents with Aldehydes, ketones, Ester and Epoxide.

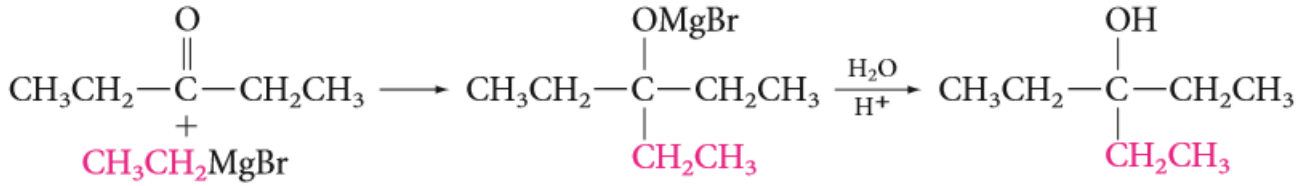
A) Grignard reagent with aldehydes and ketones



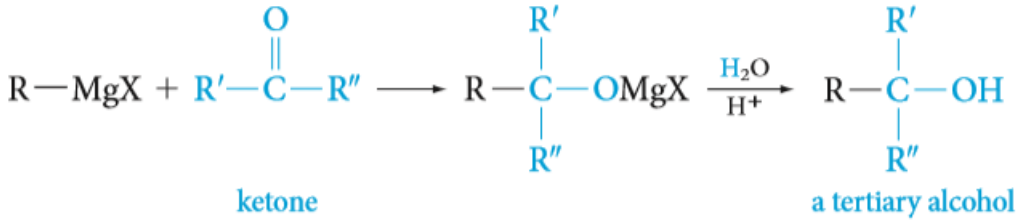


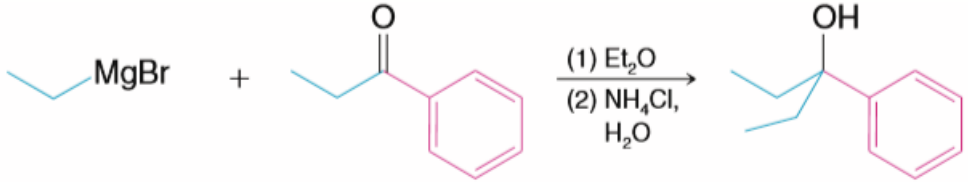
Other aldehydes give secondary alcohols.





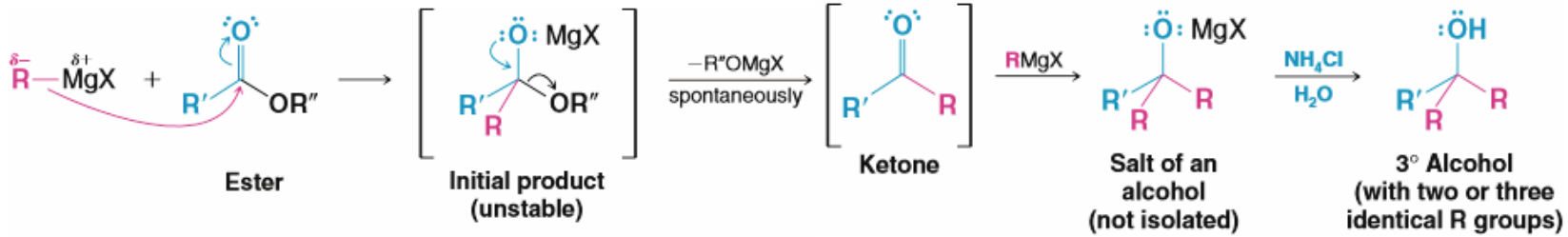
Ketones give tertiary alcohols.

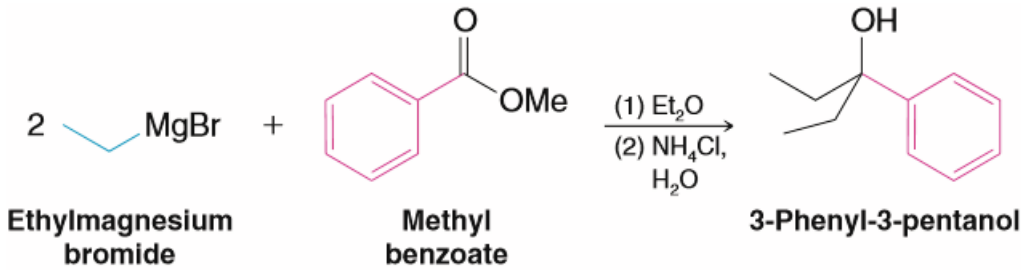




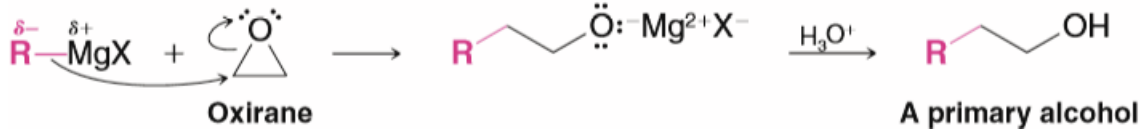
Preparation Of Alcohols

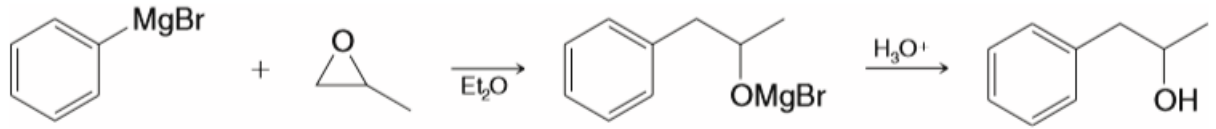
B) Grignard reagents with Ester





C) Grignard reagents with Epoxide (Oxiranes)

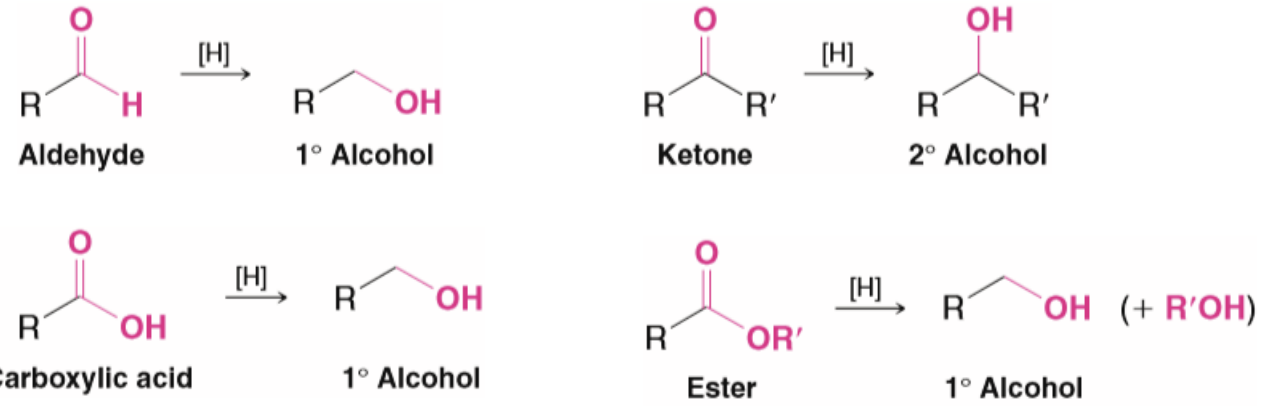


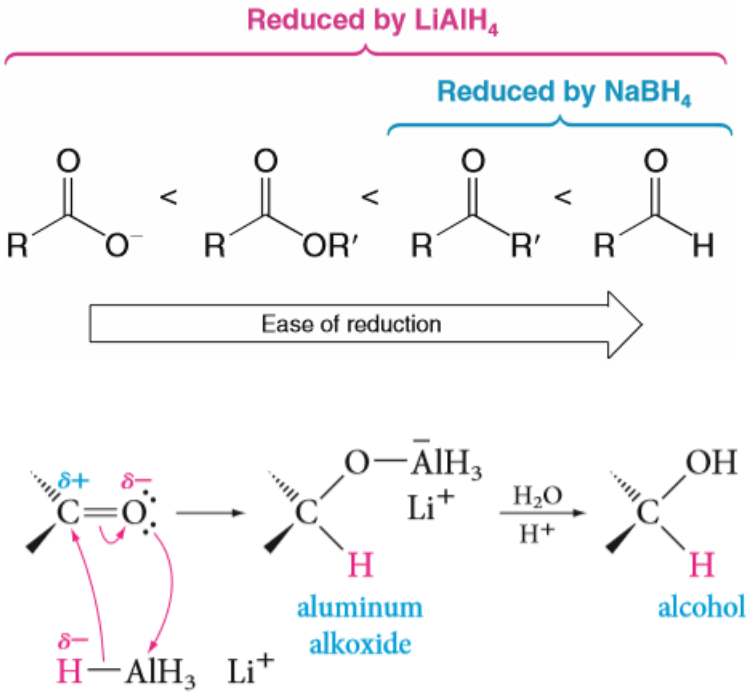


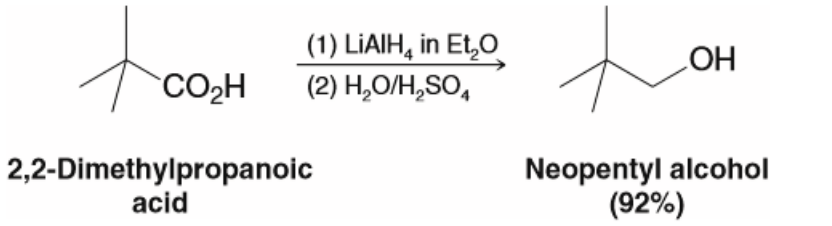
Preparation Of Alcohols

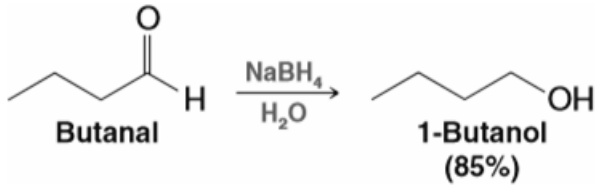
4- preparation of alcohols via Reduction reaction

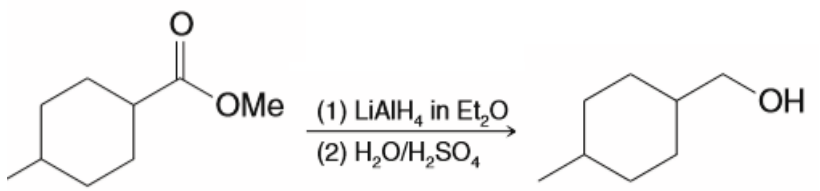
- By hydrogenation of the carbon–oxygen double bond.
- sodium borohydride ($NaBH_4$) reduce carbonyl groups (aldehydes, ketones).
- lithium aluminum hydride ($LiAlH_4$) reduce all kind of carbonyl groups.

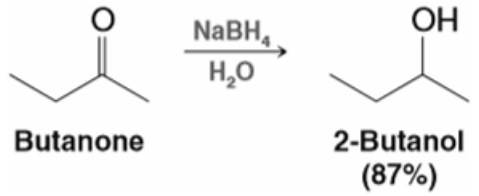












Reactions Of Alcohols

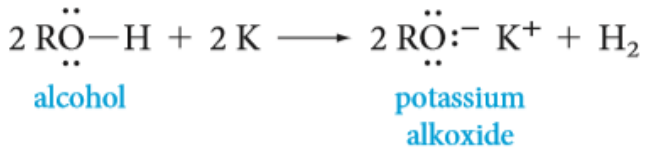
The reactions of alcohols have mainly to do with the following:

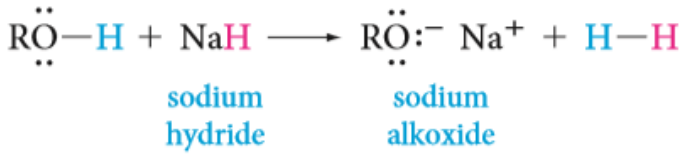
- The hydrogen atom of the hydroxyl group is weakly acidic.
  - Preparation of alkoxides
  - Preparation of Esters (Fisher esterification)
- The oxygen atom of the hydroxyl group is nucleophilic and weakly basic.
  - Oxidation Reactions
- The hydroxyl group can be converted to a leaving group so as to allow substitution or elimination reactions.
  - Conversion of Alcohols into Alkyl Halides
  - Preparation of Ethers
  - Preparation of alkenes

Reactions Of Alcohols

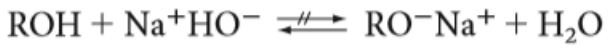
1. Preparation of alkoxides

They can be prepared by the reaction of an alcohol with sodium or potassium metal or with a metal hydride.

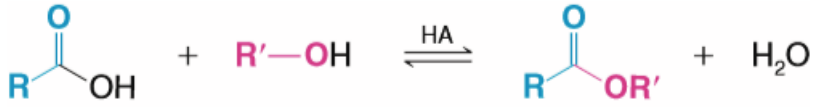


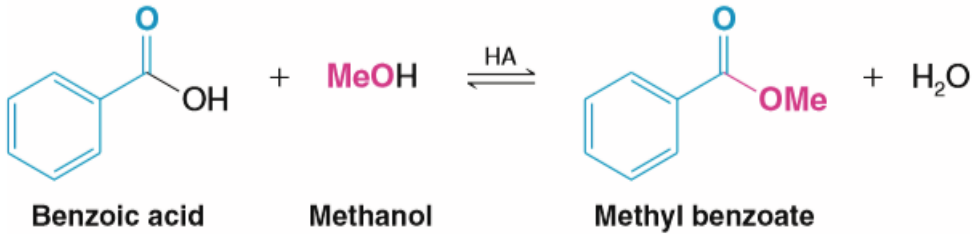


Hint:



2- Preparation of Esters: Acid-catalyzed esterification (Fisher esterification)



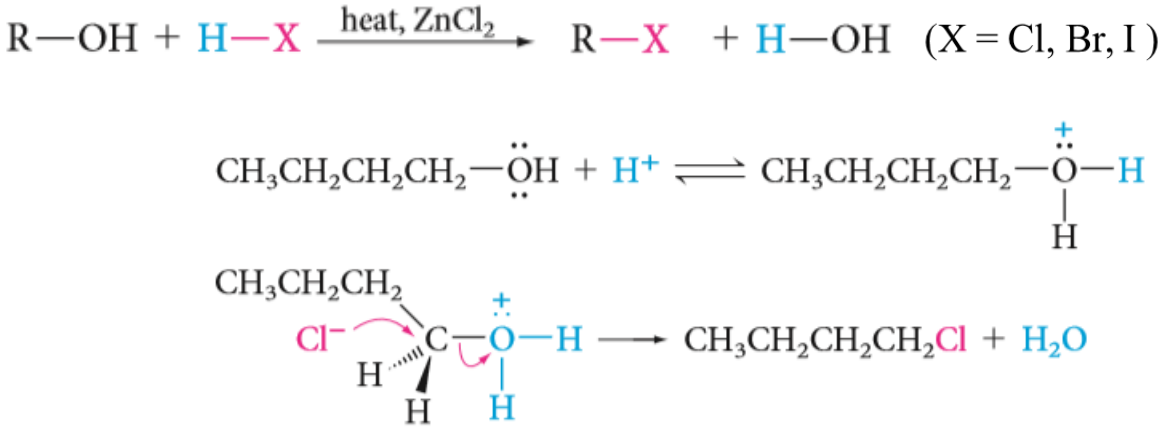


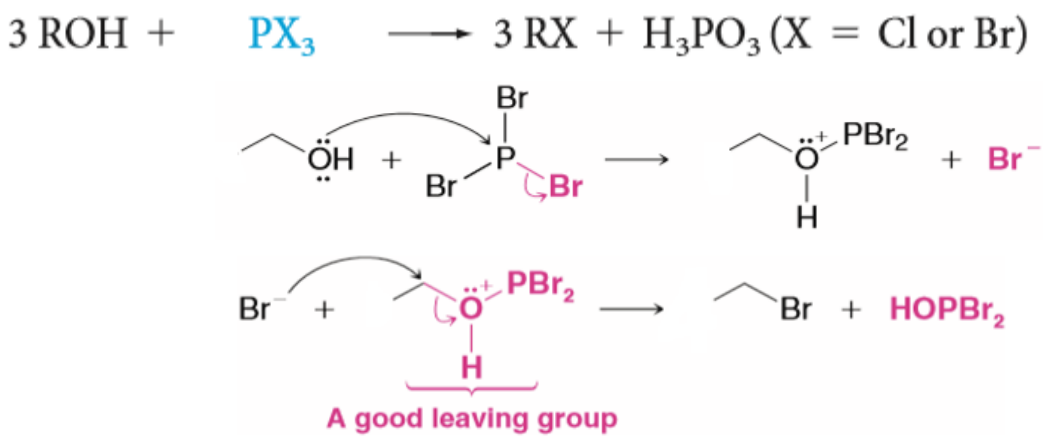
Reactions Of Alcohols

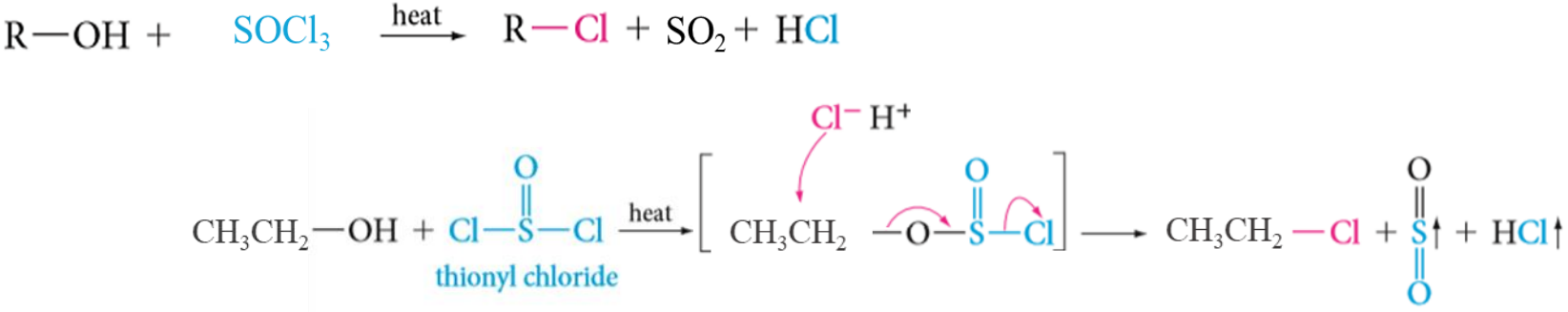
3- Conversion of Alcohols into Alkyl Halides: S_N1 or S_N2

The most commonly used reagents for conversion of alcohols to alkyl halides are the following:

- Hydrogen halides (HCl, HBr, Hl)
- Phosphorus tribromide (PBr_3)
- Thionyl chloride ($SOCl_2$)

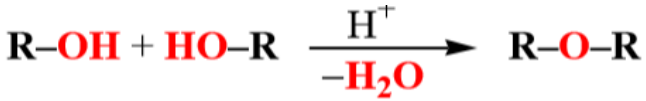


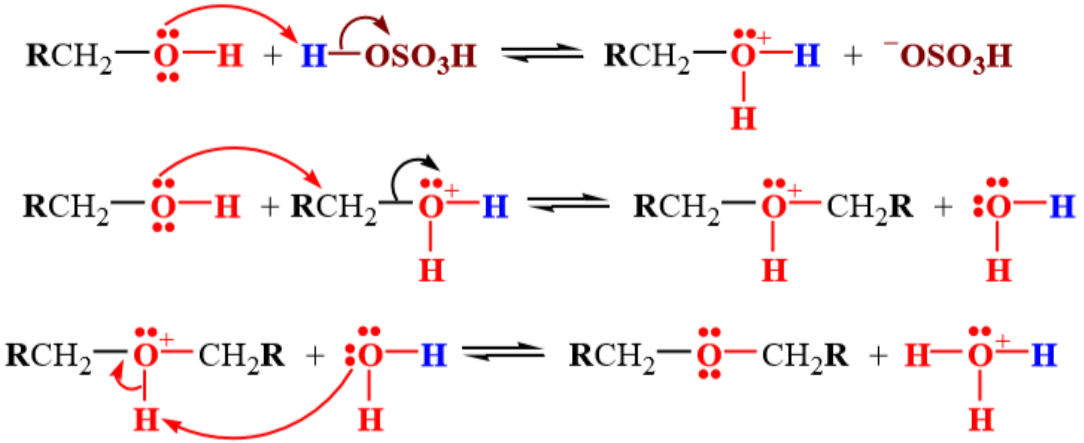




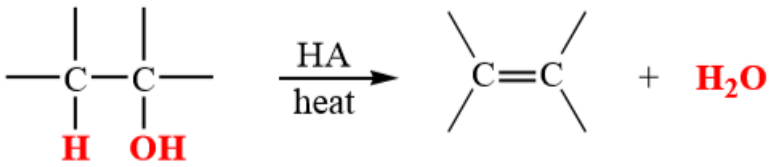
Reactions Of Alcohols

4- Preparation of Ethers

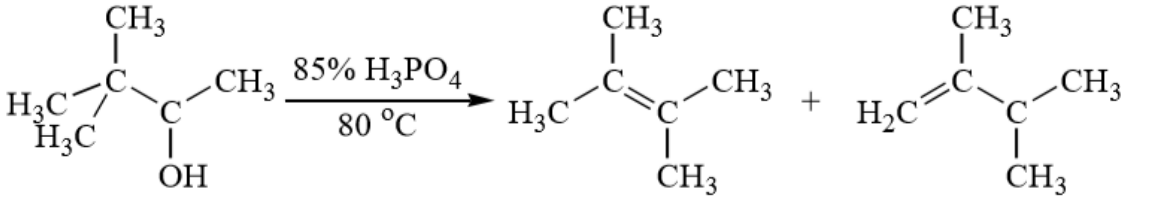




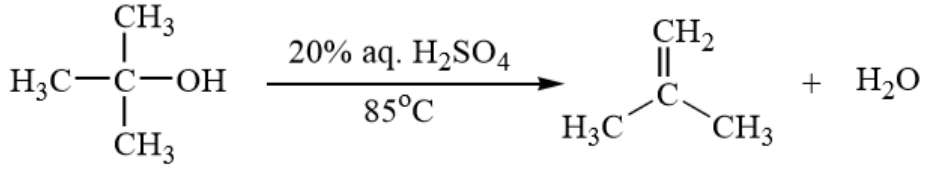
5- Elimination Reaction: Preparation of alkenes (E1 or E2)



Hint: Rearrangement



3,3-Dimethyl-2-butanol → **2,3-Dimethyl-2-butene (80%)** + **2,3-Dimethyl-1-butene (20%)**



***tert*-Butyl alcohol** → **2-Methylpropene (84%)**

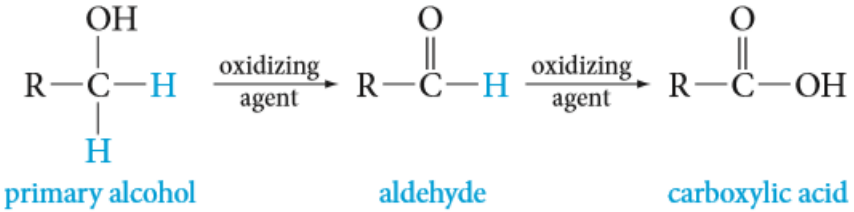
Reactions Of Alcohols

6. Oxidation of Alcohols

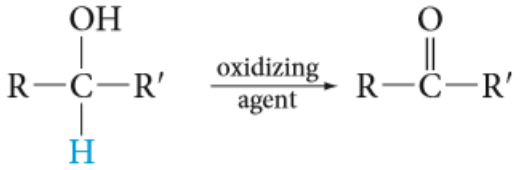
Strong oxidizing agent

Potassium permanganate $KMnO_4$,OH^-/ H_3O^+

Chromic oxide CrO_3 / H_2SO_4 (H_2CrO_4 Jones' reagent)



primary alcohol — aldehyde — carboxylic acid



secondary alcohol — ketone

No reaction

Tertiary alcohol

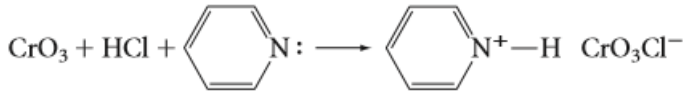
Weak oxidizing agent

Chromic oxide CrO_3 / pyridine

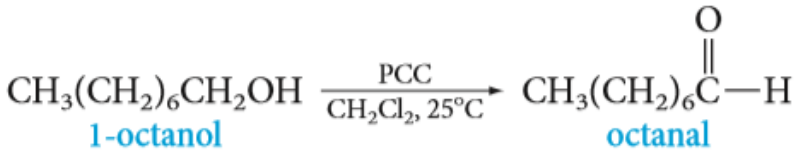
Pyridinium chlorochromate PCC / methylene chloride CH_2Cl_2

Hint:

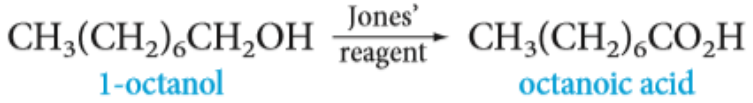
PCC is prepared by dissolving CrO_3 in hydrochloric acid and then adding pyridine:



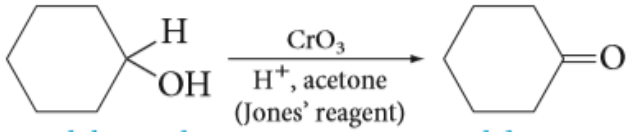
pyridine — pyridinium chlorochromate (PCC)



1-octanol — octanal



1-octanol — octanoic acid



cyclohexanol — cyclohexanone